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A Rare Thermochromic Zwitterionic Nickel(II) Complex of the Bulky Alpha Ligand 1,2-Bis-(di-^{t}butylphosphinomethyl)benzene

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Abstract: The reaction of the bulky ligand 1,2-bis-(di-tert-butylphosphinomethyl)benzene,**1** with [Ni(DME)Cl$_2$], **3**, DME = 1,2-dimethoxyethane, at room temperature over extended periods, affords the new blue Zwitterionic complex [(1,2-C$_6$H$_4$-CH$_2$$\underline{P}^{t}Bu_2$-2-C$_6H_4$-CH$_2$P(H)^{t}Bu$_2$)$_2$NiCl$_3$], **4**, which contains a phosphonium group and an anionic nickel trichloride. This complex decomposes in alcohols such as methanol and the solution turn yellow. A discussion of the possible mechanism leading to the observed product is presented. Key to this is identification of the source of the phosphonium proton, which we speculated to arise from trace water in the initial nickel complex. To prove that trace water was present in [Ni(DME)Cl$_2$] a sample of this precursor was reacted under similar condition with anhydrous DMF alone. In addition to the known complex [Ni(DMF)$_6$)]$^{2+}$[NiCl$_4$]$^{2-}$, **5,** we identified the trans-diaqua complex [Ni(Cl)$_2$(H$_2$O)$_2$(DMF)$_2$], **6**, which proved the presence of trace water. Interestingly in dimethylformamide [(1,2-C$_6$H$_4$-CH$_2$$\underline{P}^{t}Bu_2$-2-C$_6H_4$-CH$_2$P(H)^{t}Bu$_2$)$_2$NiCl$_3$] exhibits thermochromic properties: an ambient temperature pale blue solution changes colour reversibly to yellow on cooling. This behaviour is specific to DMF and is related to the solvato-chromic behaviour exhibited by related DMF nickel complexes. A discussion of the NMR spectra of compound **4** in a range of solvents is presented. The structures of the previously prepared molybdenum complex, [1,2-(C$_6$H$_4$-CH$_2$$\underline{P}^{t}Bu_2$)$_2$Mo(CO)$_4$] and the bis-(phosphine sulfide) of the ligand, [1,2-(C$_6$H$_4$-H$_2$P(S)^{t}Bu$_2$)$_2$], **5**, are described for structural comparative purposes.

Keywords: metal-complex; Zwitterion; nickel; thermochromic; phosphine; alpha; complexation; crystal; structure; DMF; self-assembly; synthesis

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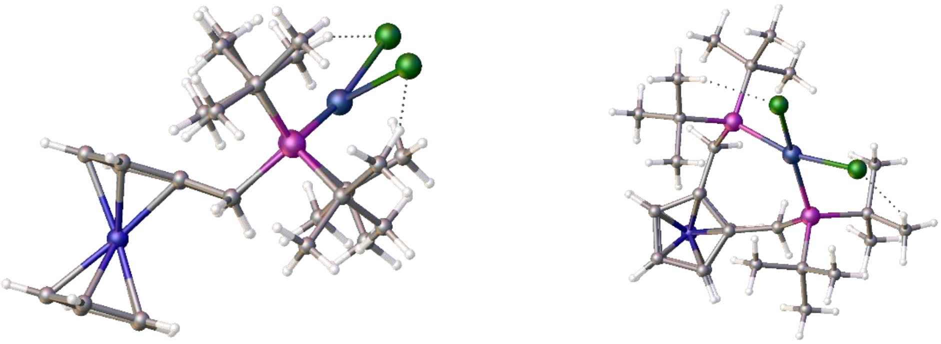
1. Introduction

The coordination chemistry of nickel (II) dichlorides with bidentate phosphines is one of the most studied areas of co-ordination chemistry with the variation in coordination geometries [1–3] between square planar and tetrahedral [4,5] being used as a vehicle to teach the differences between high and low spin complexes.[6,7] In most cases the colour of a metal complex is enough to assign whether the complex is low or high spin: larger energy gap (low spin) means the colour of the complex is the complementary one i.e. blue or green wavelengths missing therefore a yellow orange or red. Some complexes such as [Ni(PPh$_3$)$_2$Cl$_2$] exist in both coordination modes depending on the solvent it was prepared in. In rare cases a complex may be observed as a Zwitterion which is the subject of this work. The ligand we used was 1,2-bis-(di-^{t}butylphosphinomethyl)benzene, [8–10] **1**, which is the classic so-called alpha ligand.[11] This ligand was first reported and developed by Pringle's group and its synthesis and use remains seminal in the field of catalysis.[12] We have extensive experience in the coordination of these ligands particularly the ferrocene class.[13–15] The palladium coordinates to the phosphorus atoms of the ferrocene alpha ligand, *butphos*, **2**, in a square planar fashion, Figure 1. [13] The side on views indicate the ligand arms flank the palladium, in a sterically crowded environment.



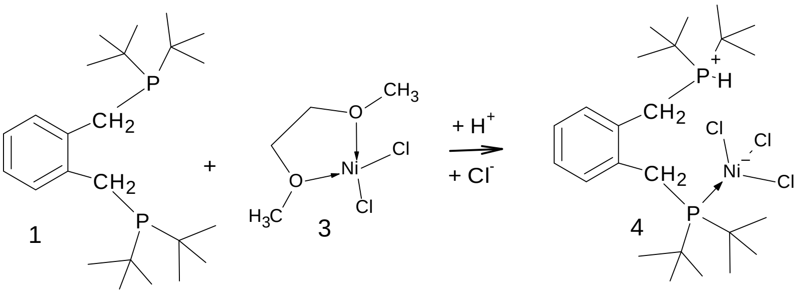
(**a**) (**b**)

Figure 1. Side and top views of the crystal structure of $[\{1,2\text{-}\eta^5\text{-}C_5H_3(CH_2P^tBu_2)_2\}Fe(\eta^5\text{-}C_5H_5)PdCl_2]$, [(*butphos*)$PdCl_2$]* showing the square planar coordination mode, [13]. (*solvent omitted).

As part of a model study, it was decided to initially examine the complexation reaction of nickel with the simple alpha ligand. Clearly this is a very important research activity simply because the development of a nickel-based catalyst of either the *alpha* ligand or the *butphos* ligand for acrylic production would be much cheaper than the current technology. Much is known about the similar square planar coordination chemistry of ligand **1** with palladium and platinum as these complexes are useful industrial catalysts, [16,17], but less so with nickel, [18].

2. Results and Discussion

With this information in hand the reaction of 1,2-bis-(di-*tert*-butylphosphinomethyl)benzene,**1** with hydrated nickel chloride in alcoholic solvents, under reflux, was attempted but this led only to amorphous yellow powders. However, when a solution of the ligand is added to the $[Ni(DME)Cl_2]$, **3**, (DME = dimethoxyethane), complex [19] in dichloromethane the solution develops a blue colour and when left for several days blue crystals begin to grow. We had anticipated the formation of red crystals which would have indicated the formation of the square planar complex or deep blue/green crystals which would indicate a tetrahedral complex. The pale blue crystals were collected after a minimum of 2 weeks and examined by single crystal diffraction; it is a rare Zwitterionic compound which accounts for its poor solubility in organic solvents. The product complex was identified as compound **4**, Figure 1.



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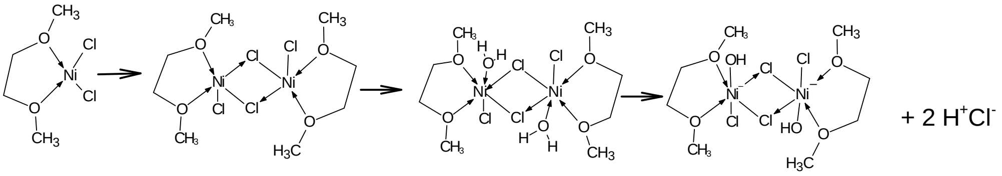
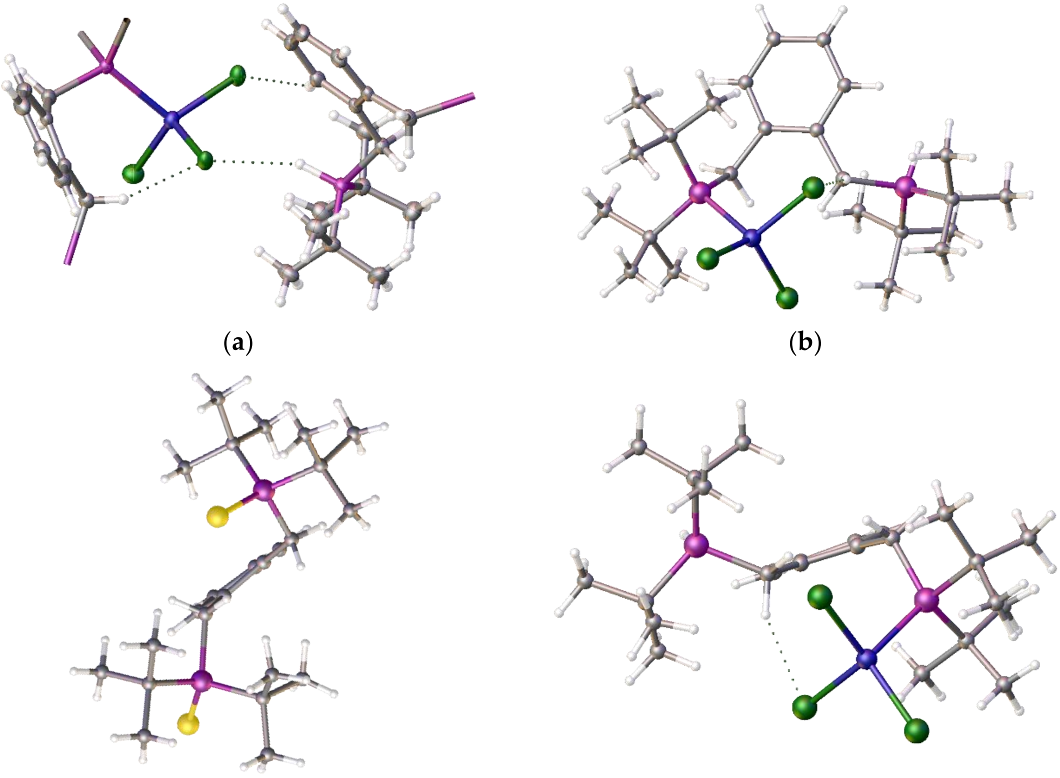


Figure 1. Schematic showing the formation of $[C_6H_4\text{-}CH_2\underline{P}{}^tBu_2\text{-}2\text{-}C_6H_4\text{-}CH_2P(H){}^tBu_2)_2NiCl_3]$, **4.** Crucial to this complexation is the addition of a proton and a chloride ion, (HCl). In the lower graphic one of the many possible modes of formation of HCl is shown; the key to this is the reaction of water with $[Ni(DME)Cl_2]$, **3**.

Only one phosphine is bound to nickel which has 3 chloride ligands attached in pseudo tetrahedral coordination, Figure 2, while the other phosphorus is protonated, forming a phosphonium pendant arm.



(**a**) (**b**)

(**c**) (**d**)

Figure 2. Views of the crystal structure of $[(C_6H_4\text{-}CH_2\underline{P}{}^tBu_2\text{-}2\text{-}C_6H_4\text{-}CH_2P(H){}^tBu_2)_2NiCl_3]$, **4**, w.r.t benzene ring, (a) cutaway showing the P-H…Cl and C-H…Cl interaction between neighbouring molecules, (b) top view(c) comparison between the ligand, shown as disulfide, $[1,2\text{-}(C_6H_4\text{-}H_2P(S){}^tBu_2)_2]$, **5**, with compound **4** (d) both showing the pendant arms above and below the benzene ring plane.

The Cl-Ni-Cl angles are 101.011(32), 120.882(32), 109.770(29) degrees respectively, while there are two close contacts between a chloride and proton on the phosphorus (2.7091(3) Å) and a chloride and a proton on the phenyl ring (2.794(7) Å), along with the internal close contact (fig 2a) of a chloride and methylene proton (2.4747(9) Å). In the structure the pendant arms of the ligand lie above and below the benzene ring, which is the same orientation observed in both the free ligand and its disulfide which is shown, for comparison, in Figure 2c. The origin of the additional proton and the additional chloride on nickel is unclear, but we propose that the chloride ion though is likely to originate from the excess nickel complex, and that the proton probably originates from trace water as the starting nickel complex is highly hygroscopic. The product complex decomposes in methanol and forms a pale-yellow solution/slurry. It is sparingly soluble in chloroform, dichloromethane, tetrachloroethane and DMF and forms a pale blue solution at room temperature. On cooling the solution in DMF to -20^{o}C, the blue colour (λ_{max}, ~621nm) changes to yellow (λ_{max}, ~ 417nm) reversibly. (see Figure 3). It is likely that DMF reacts reversibly with the nickel centre as it is a hard Lewis base with a low pKa. Interestingly $[(C_6H_4\text{-}CH_2\underline{P}{}^tBu_2\text{-}2\text{-}C_6H_4\text{-}CH_2P(H){}^tBu_2)_2NiCl_3]$, is a complex which crystallised well in regimented fashion in local magnetic fields, which was examined in a separate study we were involved in. [20]

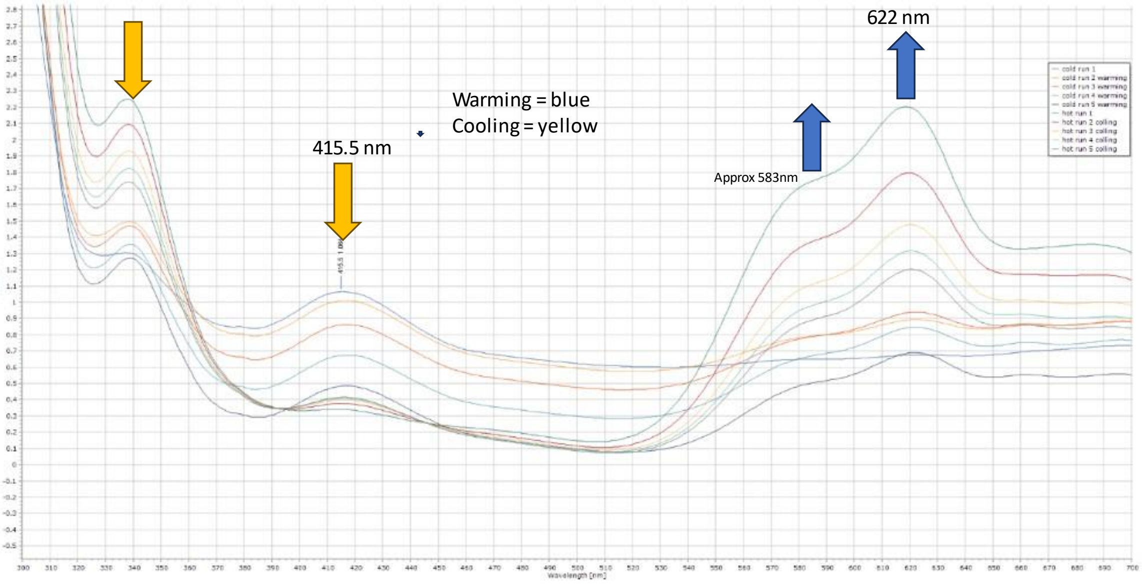
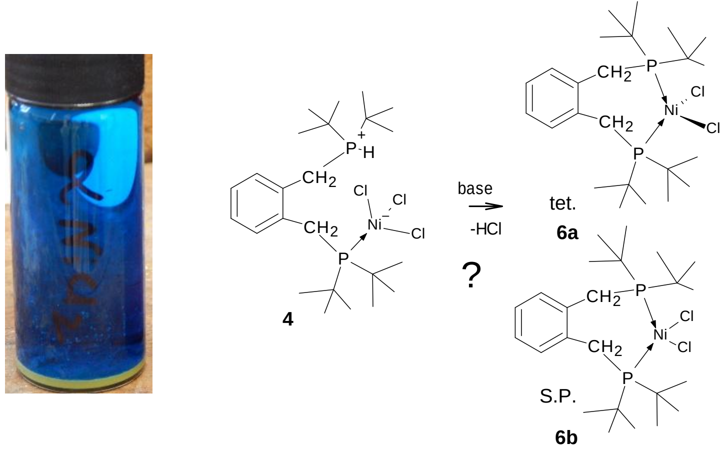


Figure 3. Compound **4** saturated solution in *dmf*; U.V spectra, warming above and below ambient. Temperature showing thermochromic nature from blue to yellow.

By looking at the structure it might be envisaged that compound **4** would react under basic conditions to produce either the square planar or tetrahedral complex, Figure 4, hence closer examination by NMR is warranted. Excepting the obvious steric crowding, it is not immediately clear why one of these chelate complexes does not form under the conditions used since we have successfully used this synthetic method for the preparation of related nickel phosphine complexes. [21]

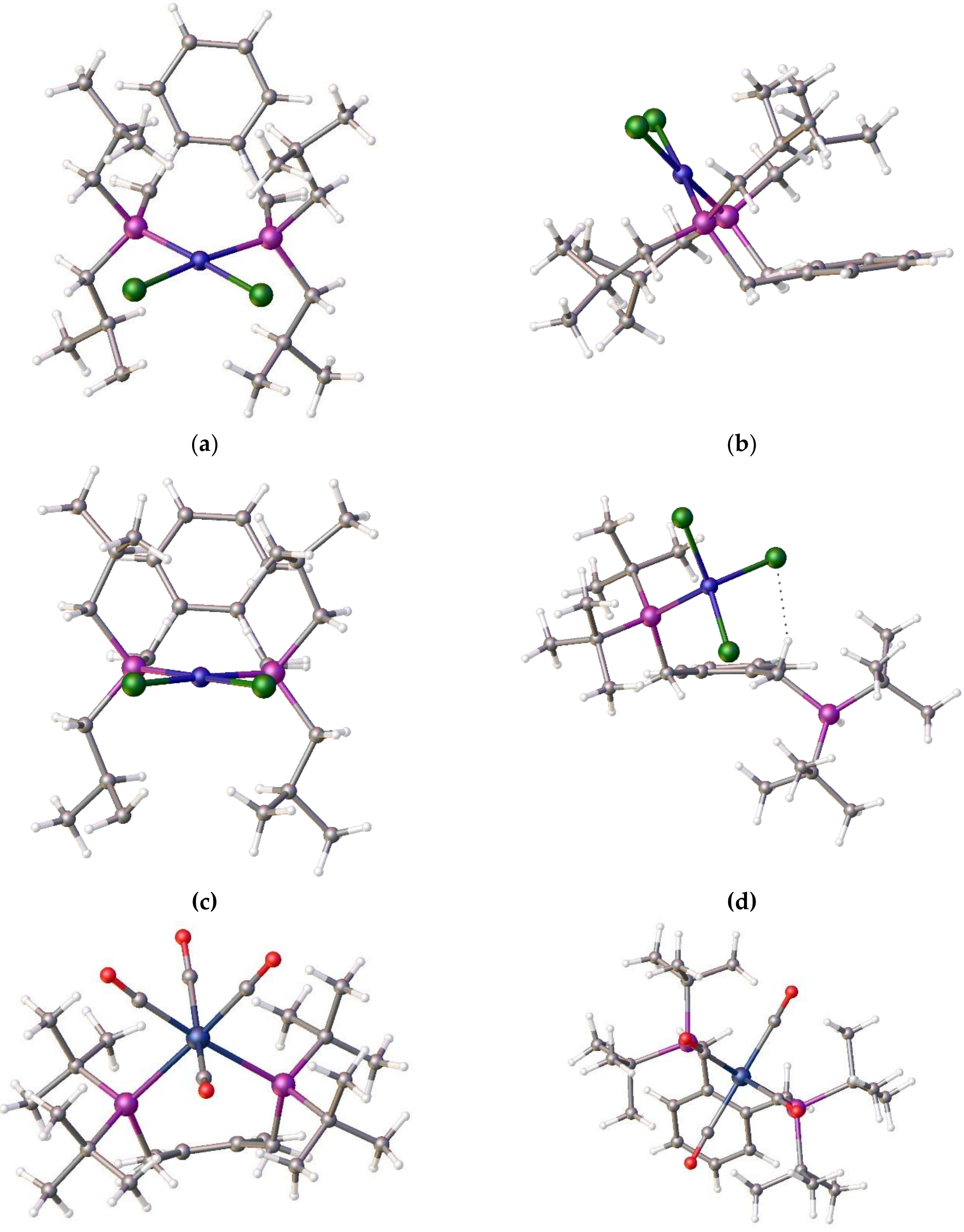


(**a**) (**b**)

Figure 4. (a) mid blue crystals of compound **4** forming on vial wall with the yellow/ochre powder of compound **3** on the bottom, (b) schematic showing that deprotonation of compound **4** with a base to obtain the chelate complex(es) should be possible.

2.1. Structural Comparisons

To understand the reason for the formation of compound **4** and not the chelate complex we decided to compare the product structure with related structures within our portfolio. During these coordination studies we have non-definitive evidence for the formation of the anticipated square-planar Ni-alpha complex as small red crystals which were isolated during one of our room temperature coordination reactions, however the initial crystallographic results indicated a disordered structure. However, we note that we have been able to determine the structure of the isomeric red nickel dichloride complex, **7**, of the related isomeric ligand $[1,2\text{-}C_6H_4\text{-}(CH_2P^iBu_2)_2]$, **8**. The structure is disordered but it clearly shows that the nickel adopts a square planar coordination mode, Figure 5, (a)-(c).



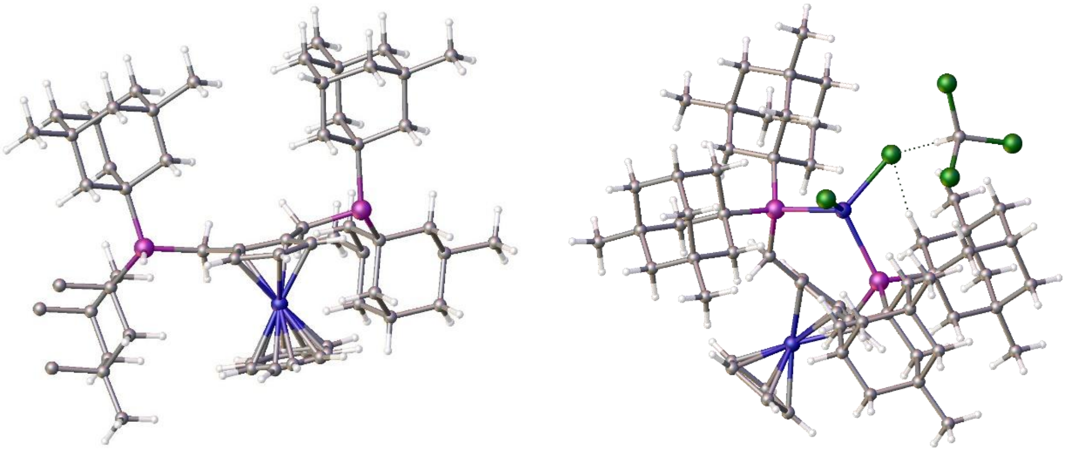
(**a**) (**b**)

(c) **(d)**

(**e**) (**f**)

Figure 5. (a) Top and **(b)** Side views of the nickel dichloride complex $[(1,2\text{-}C_6H_4\text{-}(CH_2\underline{P}^iBu_2)_2NiCl_2]$, **7**, solvent omitted, prepared from ligand and compound **3**. **(c)** and **(d)** Side by side comparison of compound **4** and **6** highlighting the difference in the pendant arms. **(e)** and **(f)** An example of ligand **4** in chelate coordination to a tungsten tetracarbonyl moiety (CCDC 2421627: full details in Supplementary Materials).

This ligand with its pendant iso-butylphosphine arms is less hindered than its tert-butylphosphine isomer which partially accounts for the difference in coordination properties and therefore its relative ease of formation. However, this cannot be the only reason for the observed differences. An examination of the structure of the tungsten tetracarbonyl complex of ligand **1**, [22] see (e) and (f) Figure 5 visually highlights a possible reason. It is simply that the shorter bond length of the nickel-phosphine bond compared to the those of the palladium-P or tungsten-P and consequently the tighter chelate bond angles of the P-Ni-P prevents coordination. Interestingly, we had previously observed structural disorder in the chloroform solvate of the nickel dichloride complex of the *bis*-1,2-[(1,3-dimethyladamantyl)phosphino]ferrocene, **8**, which exhibited tetrahedral coordination, compared with its palladium analogue, presumably, in part, because of the shorter bond length with the very sterically bulky ligand, Figure 6.



(**a**) (**b**)

Figure 6. (a) The 1,2-bis(dimethyladamantylphosphino)ferrocene ligand, **8** (fragments removed to show structure more clearly) and b) its nickel dichloride complex, **9,** chloroform solvate. This exhibits tetrahedral coordination as well as the hydrogen bonding between the ligand and a nickel-chloride, [13].

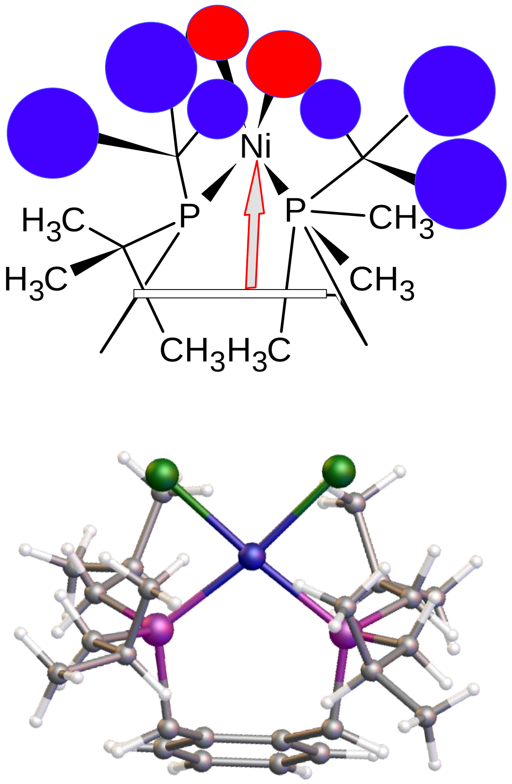
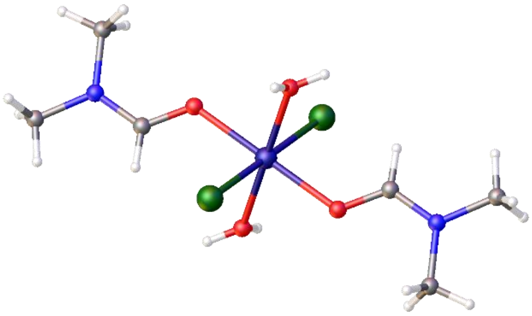


Figure 7. Front view shows the importance of the distance from the benzene ring to nickel. (shown as an arrow).

This of course leads to the question why doesn't tetrahedral coordination occur if square planar coordination is not possible due to steric crowding? The answer is not immediately obvious but maybe simply due to the mild reaction conditions used or that the shorter length of the nickel phosphine bond hinders the formation of the bidentate product. Structural comparisons between nickel and palladium complexes are complex [23,24] and clearly an extended study of a range of related ligands is warranted. Clearly the importance of the geometric parameters around the metal are important and will affect any catalytic reaction [25]. To highlight the importance of these structures a recent study using a chiral variant of this ligand class has recently been used in asymmetric hydrogenation of α-substituted acrylic acids to give chiral alpha-substituted propionic acids. In this case the catalyst was prepared in situ using nickel acetate as a precursor. [26] The next question we need to address is to confirm the source of trace water required in the synthesis, which is examined next.

2.2. Examination of the Reaction of DMF with in [Ni(DME)Cl$_2$], Looking for Source of Trace Water

To this point we have not proven that there is trace water present in the precursor, [Ni(DME)Cl$_2$], which could act as a source of the proton in the Zwitterionic complex. Therefore, we decided to examine the reaction of DMF with [Ni(DME)Cl$_2$] alone. It is known that complex equilibria exist in DMF solutions of nickel chlorides and thus DMF binding to nickel may occur. This will also have a bearing on the observed thermochromic properties of the product. Two complexes were formed in this room temperature reaction using anhydrous DMF. The first was the previously reported octahedral hexadimethylformaldehydo-nickel tetrachloronickelate, $[Ni(DMF)_6)]^{2+}[NiCl_4]^{2-}$, **8**, [27] which we crystallographically characterized (CCD Deposition Number: 2421634, full data given in the Supplementary Materials). This confirms that DMF readily coordinates to the nickel centre (to give $[Ni(DMF)_6)]^{2+}$), and it also confirms that chloro- ligands are transferred, under ambient conditions, between nickel centres (to give $[NiCl_4]^{2-}$) in DMF thus confirming the source of the additional chloride. The second complex which was identified was the all *trans*-di-aqua-bis-dimethylformaldehydo-dichloro nickel (II), $[Ni(H_2O)_2(DMF)_2 Cl_2]$, **9**, Figure 5. (2017ncs0366c; CCDC 2421635). A detailed literature search indicated this complex has since been isolated elsewhere, together with $[Ni(DMF)_2(H_2O)_4]Cl_2{\cdot}2H_2O$ [28]. This complex exists as hydrogen bonded ribbons and cutaway sections of a packing diagram are also shown in Figure 5. This complex completes a series of complexes of aqua nickel complexes as the related nickel(II), trans-$[NiCl_2(H_2O)_4]{\cdot}2H_2O$ had been previously reported, [29]. More importantly for this work though, it confirms the presence of trace water in the precursor. Thus, we have established the likely sources of the additional H^+ and Cl^-.



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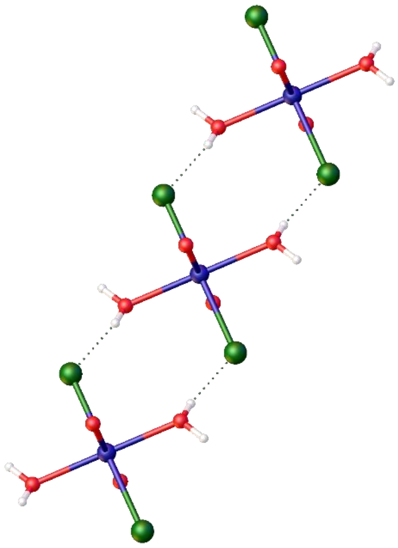
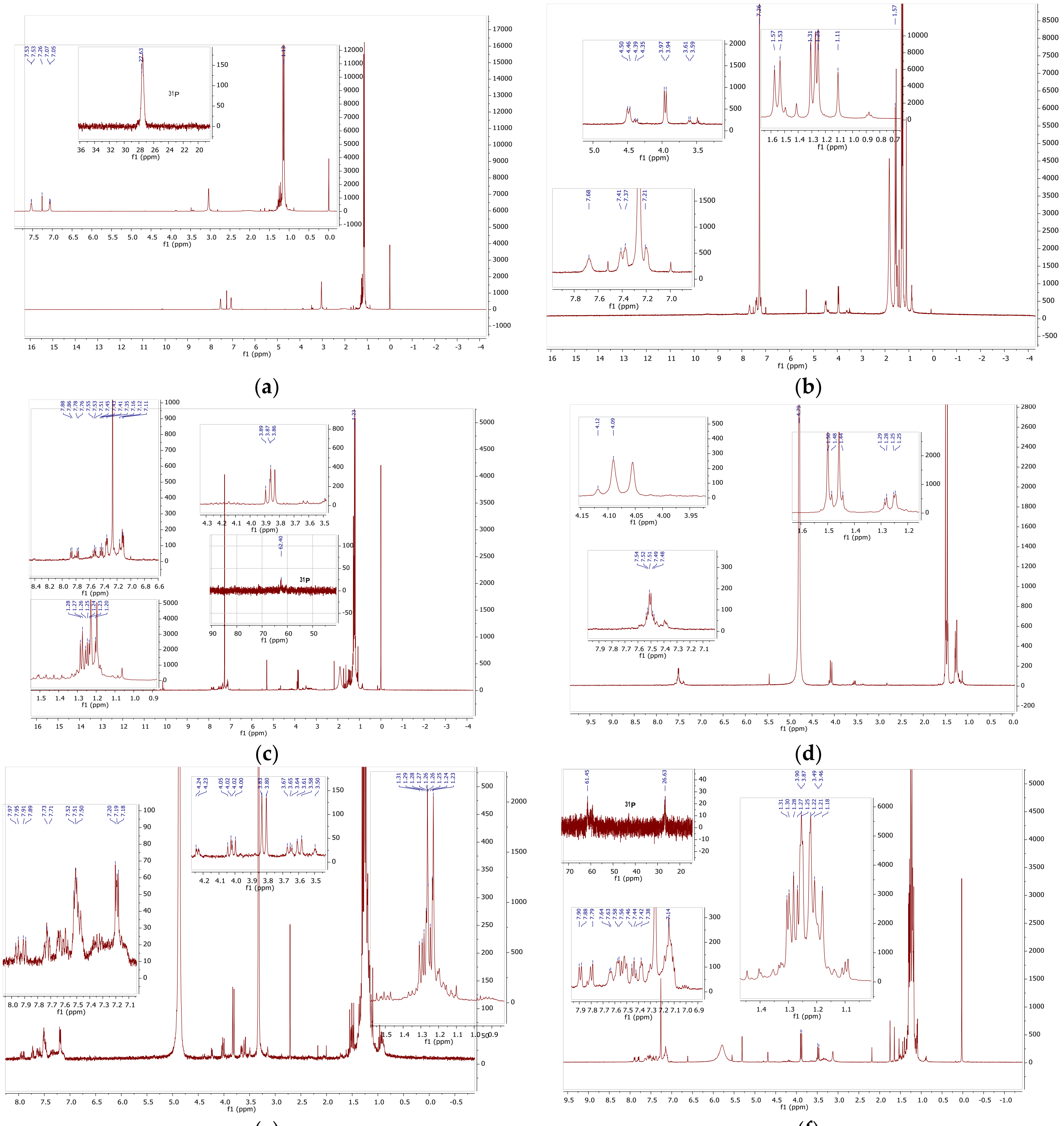


Figure 8. The crystal structure of the *diaqua-* complex, *trans*-[Ni(Cl)$_2$(H$_2$O)$_2$(DMF)$_2$], **9**, formed from [Ni(DME)$_2$Cl$_2$], and DMF at room temperature and its partial packing diagram showing the hydrogen bonding between molecules.

2.3. NMR Spectroscopic Examination of Compound **4**

To obtain more clarification proton and phosphorus NMR spectra of the complex were run in a range of solvents. In some solvents only broad resonance were observed, which generally meant that there were equilibria involving the solvent, and in other solvents there was clearly complex decomposition, nevertheless some useful data were obtained which are visually summarized in Figure 9. The low solubility in all solvents studied hinders the measurements but general conclusions may be drawn. Solvents which themselves can act as bases or ligands interact with the compound **4**, in a more complex fashion. This is not surprising given we have already observed thermochromic behaviour in DMF. In all cases there is considerable resonance overlap in the aryl region and in the alkyl-methyl regions of the spectra, however the methylene region (approx. 2.5-4.5 ppm) is relatively clear of additional resonances and is a useful diagnostic. The protons of the -CH$_2$- spacer in the ligand are observed at ca 3.4 ppm, while that of the mono-protonated ligand, which we generated independently, (ligand **1** was treated with 1,1,2,2-tetrabromoethane, which generates HBr in situ in the presence of alcohols, amine and phosphines [30]) is observed at ca 4.5 ppm. In chloroform-*d*, two groups of methylene proton are observed, the first at 3.96 ppm which we assign to those on the nickel bonded arm and the second at 4.48 ppm, (slightly broader) which we assign to those on the protonated phosphorus arm. The tert-butyl resonances of these are seen at 1.29 and 1.55 ppm respectively. The four aryl resonances are observed between 7.2 and 7.7 ppm. To observe the decomposition a sample in chloroform was treated with D$_2$O. In this case, there are two methylene resonances which are overlapped at 3.86 and 3.88 ppm. In addition, there are two sets of very low intensity multiplets at ca 3.3 and 4.3 ppm. All methyl resonances are overlapped between 1.1-1.3 ppm. In the aryl region there appear to be two groups of resonance, one set from an unsymmetrically substituted benzene ring (2 triplets, 2 doublets), and a second set of multiplet resonances at 7.12 and 7.35 ppm while in the phosphorus NMR there are again two sets of resonances one corresponding to that of the ligand at ca 27ppm and one set at ca 61.5 ppm. It is clear there is partial delegation on addition of D$_2$O but also there are new products formed. In neat D$_2$O the spectra are complex: there are at least 6 methylene resonances (therefore at least 3 compounds) and several overlapped aryl resonances, 7.1-7.6 ppm, while all tert-butyl resonances are overlapped. In deuterated methanol there is similar decomposition. In this case the one weak phosphorus resonance was observed at 65.4 ppm. In the case of the diagnostic methylene resonances; there is one large doublet (3.82 ppm, symmetrical compound), two smaller pairs of doublets (3.62, 4.01 ppm; 3.66,4.04 ppm, both unsymmetrical compounds and very low intensity resonance (dd, 4.23 ppm). In the ^{31}P NMR spectrum only very low intensity resonances were observed therefore a separate long acquisition time experiment was conducted,



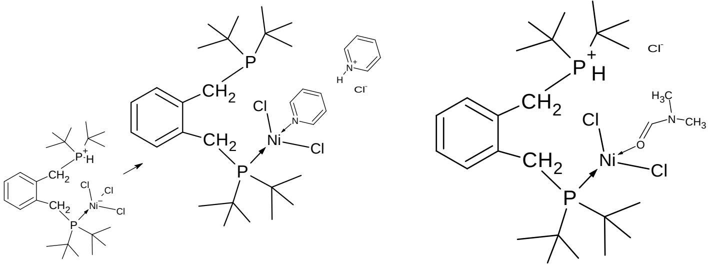
(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 9. ^{1}H NMR of compound **1.** (b) ^{1}H NMR of compound **4** in $CDCl_3$. (c) ^{1}H NMR of compound **4** in wet (D_2O) $CDCl_3$. (d), compound **4** in D_2O. (e) compound **4** in d^4 methanol, (f) ^{1}H NMR of compound **4** in $CDCl_3$ with pyridine-d^5 added.

This showed a high intensity singlet resonance at 66.6 ppm, a lower intensity 1:1:1 triplet at 64.36 ppm ($J_{P\text{-}D}$ = 182 Hz), and several low intensity singlets at 65.04, 64.20, 58.46 and 42.17ppm respectively. These were all sharp resonances, whereas a broader, yet significant, 1:1:1 triplet was observed at 38.79 ppm ($J_{P\text{-}D}$ = 70 Hz). These data show that significant proton/deuterium exchange is occurring in the sample. In one last sample pyridine-*d*^{5} was added to sample of compound **4** in chloroform-*d*; this was because the pyridine should deprotonate the phosphonium phosphorus. Two large methylene resonances were observed at 3.47 and 3.89 ppm respectively together with a series of low intensity multiplets which are centred at 3.3 and 4.2 ppm. Thus, although the deprotonation occurs a complex spectrum is the result. From these data it may be concluded that the compound **4** reacts readily with solvents which themselves may act as ligands. The chloro-ligands may be replaced or augmented to with solvent. In DMF it is likely that the DMF completely solvates the nickel centre reversibly akin to the preparation of compound **8**, shown earlier. Thus, the observed thermochromic behaviour in DMF is almost certainly a solvent related phenomenon with the chloro- ligands being displaced by DMF. [31] The first step is shown in Figure 10. Clearly it would be interesting to examine the behaviour of similar solvents towards the nickel centre. Additional NMR spectra in additional solvents may be seen in the Supplementary Materials as well as a comparison with the ferrocenyl alpha ligand. In conclusion the complex **4** is highly sensitive to solvent reactions and therefore it exhibits a high degree of lability. An examination of compound **4** using mass spectrometry (APCI on Orbitrap Instrument) was carried out; mass ions of the oxidised phosphine ligands were apparent; however, no parent mass ion was found. Interestingly however, a mass ion of (M^{+}+3) with the anticipated isotopic pattern was observed. Also present were higher mass ions with isotopic patterns centred at of m/z 938 and 971 respectively. Clearly, it would be interesting to further investigate the sold state properties of this compound.



(**a**) (**b**)

Figure 10. a) The interaction of pyridine with compound **4** showing the deprotonation of the phosphine and coordination of pyridine with nickel displacing a chloride. b) the first step in the coordination of compound **4** with DMF.

3. Materials and Methods

The protocols used in this work were essentially standard coordination and crystallization at room temperature, conditions which were developed with a view to keeping the methodology as simple as possible. We could add that crystallization is one of the main methods of self-assembly. All metal complex crystallizations were carried out with the compound dissolved in a solution of reagent grade dichloromethane with a top layer of diethyl ether added carefully. Crystals formed in all cases after the solvents co-diffused over several days. All NMR experiments were conducted at 400MHz for proton on a Bruker WH-400 instrument. Additional experimental detail is given in the Supporting Materials Section.

4. Conclusions

Although the coordination of the alpha ligand with palladium and platinum is relatively straightforward the coordination with nickel is less so- the natural propensity towards square-planar coordination may be difficult because of the steric bulk of the ligand in a relatively small coordination sphere. However, it is interesting to observe the formation of a new Zwitterionic complex. Given that there is a readily available supply of related ligands it will be of interest to observe the general trends in coordination chemistry when the synthetic method described here is applied. Clearly, given that these nickel complexes are so much cheaper to prepare than the corresponding palladium and platinum derivatives and the former of these is used in such large quantities in industrial acrylic formation, it is clearly imperative to test them in carboxy-alkylation reactions. We would encourage interested research groups to contact us to develop such work. Also, by performing the reaction in 1,1,2,2-tetrabromoethane it may be possible to add a bromine instead of chlorine to the nickel center as this compound acts as a source of HBr in the presence of phosphines. At the suggestion of reviewers, it would be extremely interesting to examine the temperature variant magnetic properties of compound **4** and its congeners. We thank the reviewers for their positive suggestions.

Supplementary Materials: Detailed NMR spectra in a range of solvents are presented. Crystallographic data for $[1,2\text{-}(C_6H_4\text{-}CH_2\underline{P}{}^tBu_2)_2Mo(CO)_4]$, $[1,2\text{-}(C_6H_4\text{-}H_2P(S){}^tBu_2)_2]$, $[2\text{-}(C_6H_4\text{-}CH_2\underline{P(H)}{}^tBu_2\text{-}1\text{-}(CH_2\underline{P}{}^tBu_2NiCl_3)]$, $[1,2\text{-}(C_6H_4\text{-}CH_2\underline{P{}^iBu_2})_2NiCl_2]$, $[Ni(DMF)_6)]^{2+}[NiCl_4]^{2-}$, $[Ni(Cl)_2(H_2O)_2(DMF)_2]$ are available as supplementary materials. CCDC 2421627 and 2421631-5 respectively also contain the supplementary crystallographic data for this paper. These CCDC data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge, CB2 1EZ. Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). Total 114 pages.

Author Contributions: I.R.B.: investigations, experimental work, writing, reviewing and editing, supervision, methodology, conception. P.N.H.: crystallography, data deposition, writing; W.C.: proofing, crystallography work, director of crystallographic facilities; S.J.C.: Director of National Crystallographic Services and project overseer; K.M.F. synthesis, thesis work; M.D. early crystallography (2004); K. S.: synthetic work and experimental work. All authors have read and agreed to the published version of the manuscript.

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